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Synthesis and structure of 1,3-bis(hydroxysilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane

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ABSTRACT

Trans-silylation reactions of $(Me_3Si)_2NH$ with $PhRSiCl_2$ (R = Me, Ph) gave $HN(SiMePhCl)_2$ (**1**) or ClMePh-SiNHSiPh_2Cl (**2**). The treatment of 1,3-dichlorodisilazane (**1** or **2**) with an equimolar amount of *n*-BuLi led to the formation of 1,3-bis(chloro-silyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane $(ClSiMePh)_2(NSiMePh)_2$ (**3**) or $(ClSiPh_2)_2(NSiMePh)_2$ (**4**), which was allowed to hydrolyze to form 1,3-bis(hydroxysilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane $(HOSiMePh)_2(NSiMePh)_2$ (**5**) or $(HOSiPh_2)_2(NSiMePh)_2$ (**6**), respectively. The cyclodisilazane monomers were characterized by elemental analysis, NMR and IR spectroscopy. Compound **3** was obtained as a 4:6 *cis*/*trans* mixture while **4** adopted *trans*-structure considering the hindrance of pendent groups. In addition, the molecular structures of *trans*-**5** and *trans*-**6** were determined by X-ray crystallographic analysis and discussed in detail.

1. Introduction

Owing to their specific structural features, *N*-silyl-substituted cyclodisilazanes have attracted increasing attention as potential complements to silicone rubber in high-temperature applications [1–6]. Despite their striking thermal stability, few reports deal with such applications due to the inherent hydrolytic instability of the silicon-nitrogen bond [7]. It has been found that the existence of bulky substituents on the silicon atoms increases the thermal and hydrolytic stability of cyclodisilazanes. Therefore, phenyl-substituted cyclodisilazanes are expected to be introduced into the backbone of linear polysiloxane chains to synthesize thermally resistant elastomers [8,9]. An important goal in this area is the synthesis of cyclodisilazane monomer [10–16] with a feasible structure. While several cyclodisilazanes bearing phenyl groups have been reported [3,17,18], few works refer to the mixed phenyl-substituted cyclodisilazanes which exhibit unique structural characteristic. The molecular structure of these cyclodisilazanes with phenyl substituents can be described as $XR_2Si[NSiMePh]_2SiR_2X$. We have recently demonstrated that these cyclodisilazanes possess favorable thermal stability with good prospects. Breed and Bao [19,20] respectively reported the preparation of $(ClSiMePh)_2(NSiMePh)_2$, which was simply characterized by ^{1}H NMR and IR absorption as indication of the presence of Si_4N_2 skeleton. However, no further evidence was described and its molecular structure remained so far unknown.

In this paper, we report the improved synthesis of 1,3-bis(hydroxysilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (**5** and **6**) and the molecular structure of *trans* isomer (*trans*-**5** and *trans*-**6**). In particular, the stepwise reactions are analyzed by the inspection of ^{29}Si NMR spectra.

2. Results and discussion

2.1. Synthesis

1,3-Dichlorodisilazanes (**1**, **2**) required for the formation of cyclodisilazanes were prepared via the trans-silylation reactions [21,22] of $(Me_3Si)_2NH$ with dichlorosilane (Scheme 1). The reaction of $(Me_3Si)_2NH$ with $MePhSiCl_2$ proceeded smoothly to give the expected 1,3-dichlorodisilazane **1**. The reaction could be accelerated while large excess of $MePhSiCl_2$ was used at high temperature. The intermediate mixed disilazane by substitution of one trimethylsilyl group was also obtained in the condition of a lower temperature or using a deficient amount of dichlorosilane. The procession was carried out easily to bring the intermediate compound of $Me_3SiNHSiRPhCl$ (**1a, 1b**) which was expected to be valuable for the synthesis of designed 1,3-dichlorodisilazane. The signal of the chloro-silyl group was observed with a high-field chemical shift in the ^{29}Si NMR spectrum (**1a**: 6.56, 1.56 ppm; **1b**:

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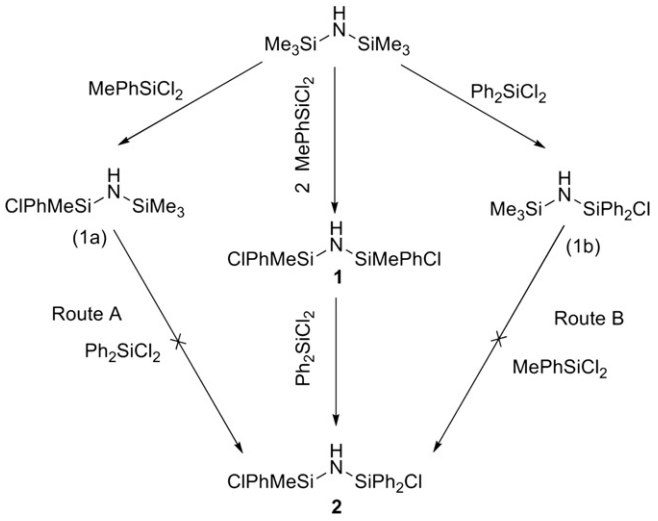


Scheme 1.

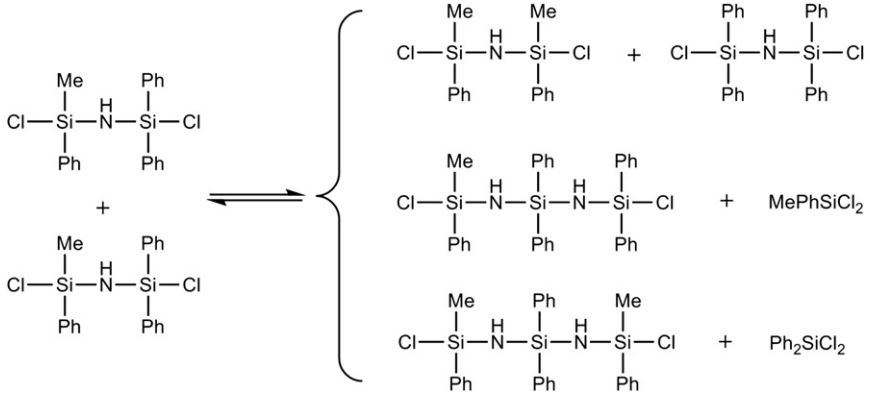
5.92, −8.23 ppm). However, our initial attempt to obtain **2** by replacing another trimethysilyl group of the intermediate compound with dichlorosilane (either route **A** or **B**) was unsuccessful. Instead, a mixture of symmetrical 1,3-dichlorodisilazane (either $HN(SiMePhCl)_2$ or $HN(SiPh_2Cl)_2$) and unreacted **1a** or **1b** was were found as the principal product of conversion. The varied substitution product revealed that there was a competition between $SiMe_3$ and SiRPhCl group for the trans-silylation reaction of the intermediate compound $Me_3SiNHSiRPhCl$ (**1a** or **1b**). From the observed reactivity, we presumed that the exchange reaction of the intermediate compound was accessible to SiRPhCl group since nucleophilic attack of Si–N bond occurred more easily when electron-withdrawing chlorine atom was attached to silicon atom. On the basis of these results, we focused our attention to the exchange reaction of 1,3-dichlorodisilazane with dichlorosilane [23]. If a large quantity of **2** was desired, this would be the method of choice. The reaction of **1** with Ph_2SiCl_2 (molar ratio = 1:1.1) successfully afforded **2**, where heating the reaction mixture over 160 °C under distilling off $MePhSiCl_2$ is required. The yield of **2** was greater than 60%, as determined by ^{29}Si NMR of the crude reaction mixture.

However, the asymmetrical 1,3-dichlorosilazane **2** remained thermally unstable and could further undergo redistribution reactions which result in a lower yield (33%) [24,25]. In fact side reactions of Si–N bond cleavage became appreciable at high temperature for the chlorine-terminated disilazane which resulted in a series of rearrangements [18]. As a result, **1** or **2** provided with reactive chloro-silyl groups could further undergo self-redistribution or react with each other. All the possible interconversions accounting for the presence of several dichlorosilazanes in the remaining crude are illustrated in Scheme 2 (inspected by ^{29}Si NMR). Moreover, such side reactions even continued during the distillation of **2**. Therefore, **2** was isolated possibly with little admixture of dichlorosilane and **1**.

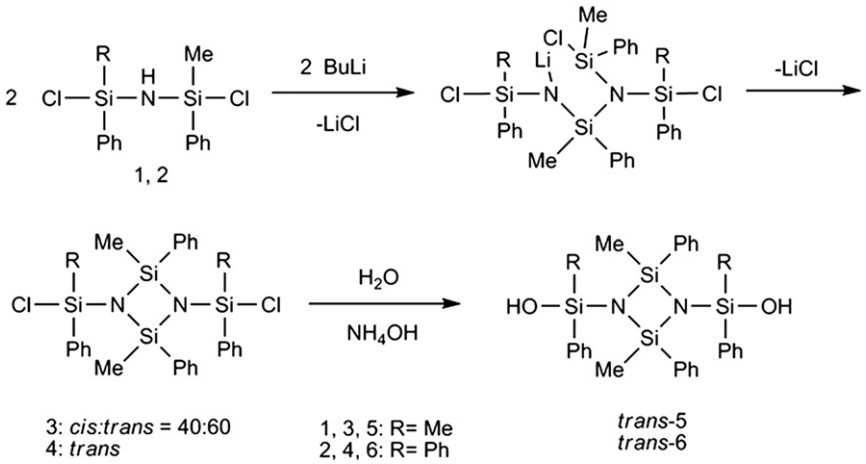
Generally, the use of butyllithium provides an advantageous route to a variety of cyclodisilazane monomers. The mechanism features primary metalation at nitrogen of a 1,3-dichlorodisilazane followed by a bimolecular condensation to a trisilylamine structure with subsequent ring closure [19]. The 1,3-bis(chloro-silyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane **3** and **4** were synthesized by stepwise reactions as shown in Scheme 3. We found that nearly quantitative conversion to such cyclodisilazanes could occur at 70 °C which offered a mild condition compared to the previously reported work [19,20]. When the ring-closure reaction of **1** or **2** was performed using an equivalent of *n*-BuLi in toluene, **3** was obtained in large quantities as a mixture of *cis*/*trans* isomers while **4** was formed as *trans*-cyclodisilazane. However, the mixed isomers of **3** turned out to be hydrolytically unstable, our attempt to isolate the *cis* and *trans*-structures by crystallization failed.

For these mixed phenyl-substituted cyclodisilazanes, isomeric structures probably appeared as a result of the transmission of substituent effects throughout the Si_4N_2 skeleton which indicated that long-range coupling could occur through silicon in the structure $C_6H_5SiCH_3$ [19]. Of particular interest was the spectrum of **3**, the mixture of *cis*/*trans* isomers was clearly observed in the ^{29}Si and ^{13}C NMR spectra.

The ^{29}Si NMR spectrum of **3** showed a chloro-silyl resonance at −2.38 ppm. As shown in Fig. 1, two stereoisomers of **3**, which are called *cis* and *trans* isomers are based on the configuration of two phenyl groups on the Si_2N_2 ring. The two phenyl groups are oriented in the same direction, the diastereomer is referred to as *cis*, whereas, when the phenyl substituents are oriented in opposing directions, the diastereomer is referred to as *trans*. Accordingly, the mixture of *cis*/*trans* isomers gave rise to two sets of signals for the endocyclic silicon atoms. The silicon resonance of *cis*-**3** (−3.10 ppm) in which the silicon-attached phenyl groups are on the same face of the Si_2N_2 ring, shifted downfield relative to the corresponding silicon atoms in *trans*-**3** (−3.46 ppm) [26] with the integrated area ratio of 4:6. The ^{13}C NMR analysis also revealed the presence of mixed isomers (*cis*/*trans* = 40/60). For *cis*-**3**, the different substituents on the pendent silicon could influence the methyl groups on the Si_2N_2 ring which are oriented in the same direction to give two



Scheme 2.



Scheme 3.

separate singlets (*cis*-**3**: 0.76, 1.36 ppm) in the ^{13}C NMR spectra possibly due to the coplanar geometry, whereas single sharp resonance assigned to the *trans* isomer (*trans*-**3**: 1.05 ppm). In contrast, the ^{29}Si and ^{13}C NMR spectrum of **4** showed only one singlet resonance for endocyclic silicon atoms (−14.80 ppm) and methyl carbon (1.40 ppm) which indicated the chemical equivalency for the *trans* isomer.

In order to explain these observations, we have considered that the nature of the substituents on the exocyclic silicons seems to have great effect on the formation of stereoisomers. The steric factors appear to influence the observed structure, particular in **3** and **4**. A mixture of *cis*/*trans* isomers was obtained in **3** as compared to **4**, where only *trans* isomer was formed. For **3**, the existence of less bulky methyl groups on the exocyclic silicons allows for less influence of steric hindrance on cyclodisilazane formation and thereby can display *cis*/*trans* isomerism. On the other hand, steric constraints around the pendent silicons with substitution of both phenyls in **4** favor the formation of *trans* configuration.

Compound **3** (mixed isomers) and **4** were subsequently converted into 1,3-bis(hydroxysilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane **5** and **6** by hydrolysis in the presence of aqueous ammonia. The substitution of two chlorine atoms was detected by ^{29}Si and ^{13}C NMR spectra which also indicated only *trans* isomers were obtained. The ^{29}Si NMR spectrum for **5** and **6** showed the silyl hydroxyl signals at −20.10 and −31.70 ppm and endocyclic-Si signals at −5.66 and −4.37 ppm, respectively. The integration ratio of the exocyclic-Si signal was fully consistent with the endocyclic-Si in the spectrum. The ^{13}C NMR spectrum of **5** exhibited single peak for methyl carbons on the ring, which can be interpreted that only *trans* isomer was left after hydrolysis.

The FT-IR spectra of the cyclodisilazane monomers (**3**, **4**, **5** and **6**) are shown in Fig. 2. The cyclic Si_4N_2 skeleton is confirmed by the existence of absorption peaks at 1116 (1118) cm^{-1} and 829 (842) cm^{-1} [13,19]. The peaks at 1015 (1018) cm^{-1} and 697 (699) cm^{-1} are typical for asymmetric stretching of Si—N—Si and Si—C symmetric stretching, respectively. The spectrum exhibits C—H stretching in the phenyl group at 3003, 3050 and 3069 cm^{-1}. A strong peak at 1427 cm^{-1} and three weak peaks at 1826, 1895 and 1960 cm^{-1} are associated with the phenyl-Si vibration. It shows a similar spectrum to its corresponding cyclosilazane with extra absorption peaks at 503 (510) and 532 (541) cm^{-1} for the stretching of Si—Cl and 3585 cm^{-1} for Si—OH.

As reported, bulky groups such as phenyl greatly decreased the reactivity of hydrolysis under acidic or basic conditions and left the Si_2N_2 ring intact [7]. However, the structure of Si_2N_2 with mixed phenyl groups especially for *cis*-**3** apparently had little effect on the hydrolysis [27]. Further reaction involving the cleavage of endocyclic Si—N bonds occurred to produce the siloxane derivatives $(MePhSiO)_{3,4}$ which were detected by ^{29}Si NMR spectra and this accounted for the low yield (47%) of compound **5**. *Trans*-**5** was formed predominantly during the hydrolysis reaction since *trans*-**3** is supposed to have greater hydrolytic stability, whereas *cis*-**3** was hydrolytically unstable and underwent complete hydrolysis with

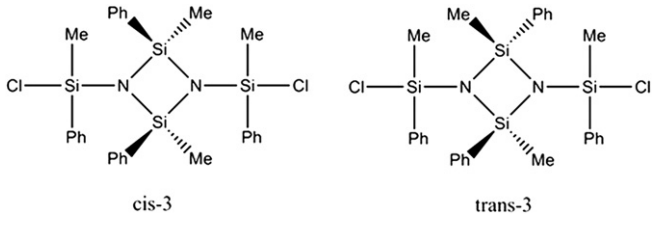


Fig. 1. Isomeric structures of *cis*-**3** and *trans*-**3**.

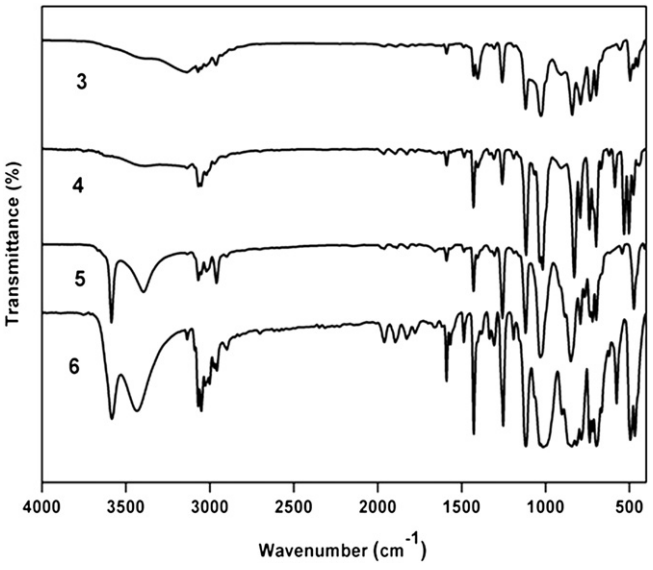


Fig. 2. FT-IR spectra of cyclodisilazane monomers (**3, 4**, **5** and **6**).

the decomposition of the Si_2N_2 ring. Consequently, we have considered that the predominant formation of *trans*-**5** is apparently attributed to the influence of steric hindrance of oriented phenyls in *trans*-**3** which could largely shield the Si_2N_2 ring from hydrolytic cleavage.

2.2. Molecular structures

The molecular structures of *trans*-**5** and *trans*-**6** are illustrated in Figs. 3 and 4. Selected bond and angle parameters are listed in the caption of the figure. The structures of *trans*-**5** and *trans*-**6** consisting a mixed substituted Si_2N_2 ring are almost similar. The cyclodisilazane forms a planar Si_2N_2 heterocycle with N-Si–N and Si–N–Si angles of 89.18°, 90.82° in *trans*-**5** and 89.23°, 91.77° in *trans*-**6,** respectively. Such values are in good agreement with the symmetrical substituted Si_2N_2 ring determined previously [28–32]. The geometry around the nitrogen atom is coplanar to within 0.04 Å and the sum of the valency angles is approximately 360°. The planarity of the nitrogen atom attached to the ring indicates delocalization of its unshared electron pair as a result of dπ–pπ interaction with Si(1), Si(2) and Si(2A)/Si(4). The Si(2) adopts a distorted tetrahedral geometry that ranges from a rather acute intraannular N-Si–N angle (*trans*-**5**: 88.81°, *trans*-**6**: 89.23°) to a comparatively obtuse extraannular C–Si–C angle (*trans*-**5**: 110.31°, *trans*-**6**: 109.97°). The orientation of the phenyl groups on the ring is represented by the torsion angle of C–Si(2)–Si(2A)/Si(4)–C (*trans*-**5**: 171.5°, *trans*-**6**: 178.5°). As expected, the plane of the phenyl groups forms *trans*-structure among the planar Si_2N_2 ring. The Si(1)–N(1) bond length (*trans*-**5**: 1.712 Å, *trans*-**6**: 1.699 Å) is significantly shorter than the Si(2)–N(1) or Si(4)–N(1) bond length (*trans*-5: 1.742, 1.753 Å; *trans*-6: 1.730, 1.754 Å). The endocyclic silicon atoms approach strikingly to each other that the transannular Si···Si distance (*trans*-**5**: 2.48 Å, *trans*-**6**: 2.50 Å) goes near to van der Waals radii of the Si–Si bond (2.32 Å in Si_2Cl_6).

3. Conclusion

We have synthesized 1,3-dichlorodisilazane **1** and **2** via a transsilylation reaction. The inspection indicates that the exchange reaction of the intermediate compound $Me_3SiNHSiRPhCl$ is accessible to SiRPhCl group. Owing to the mixed phenyl substituents attached to the Si_4N_2 skeleton, cyclodisilazane **3** was confirmed as a mixture of *cis*/*trans* isomers by ^{29}Si, ^{13}C NMR analysis. *Trans*-**5** was obtained by hydrolysis of the isomeric mixture of **3**. The molecular structures of *trans*-**5** and *trans*-**6** show that the geometrical parameters are nearly identical, which exhibit similar characteristic for the cyclodisilazane molecules of this type. Further work will concentrate on obtaining the *cis*-**5** in order to have a further understanding of its hydrolytic stability.

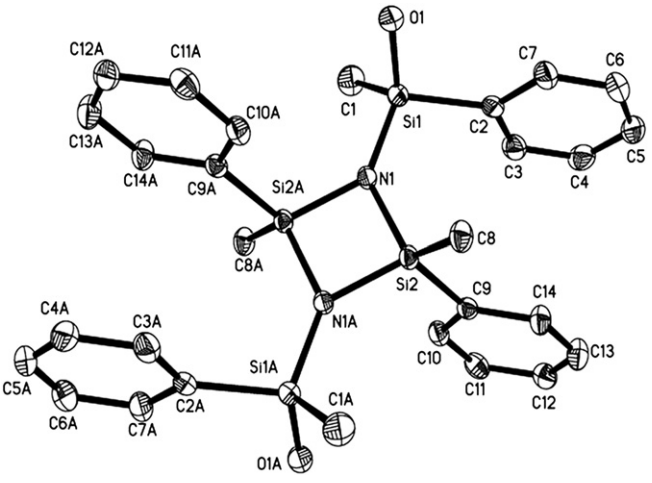


Fig. 3. X-ray crystal structure of *trans*-**5**. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si(1)–O(1) 1.634(3),Si(1)–N(1) 1.712(2), Si(2)–N(1) 1.742(2), Si(2A)–N(1) 1.753(3), Si(2)–C(8) 1.857(3), Si(2)–C(9) 1.870(3), Si(1)–N(1)–Si(2) 133.28(15), Si(1)–N(1)–Si(2A) 135.90(15), Si(2)–N(1)–Si(2A) 90.82(12), N(1)–Si(2)–N(1A) 89.18(12), N(1)–Si(2)–C(8) 114.65(14), N(1)–Si(2)–C(9) 113.39(12), C(8)–Si(2)–C(9) 110.31(14).

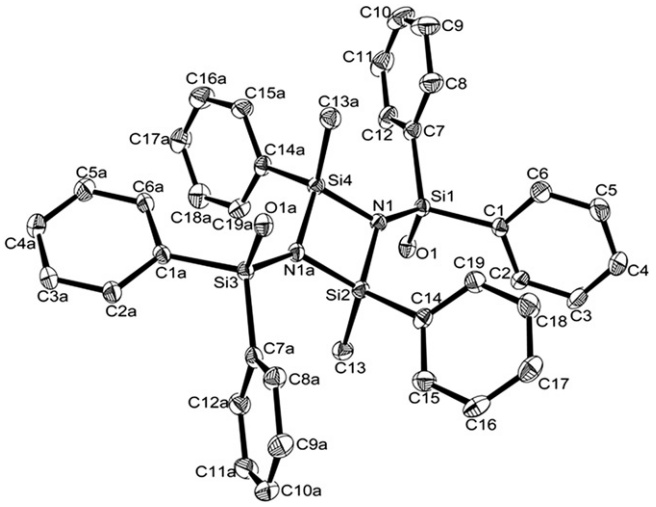


Fig. 4. X-ray crystal structure of *trans*-**6.** Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si(1)–O(1) 1.627(2), Si(1)–N(1) 1.710(3), Si(2)–N(1) 1.754(3), Si(4)–N(1) 1.730(3), Si(2)–C(13) 1.855(4), Si(2)–C(14) 1.864(4), Si(2)–N(1)–Si(4) 91.77(15), N(1)–Si(2)–N(1A) 88.22(15), Si(1)–N(1)–Si(4) 132.62(18), Si(1)–N(1)–Si(2) 132.98(18), N(1)–Si(2)–C(13) 113.30(16), N(1)–Si(2)–C(14) 113.84(16), C(13)–Si(2)–C(14) 107.27(17).

4. Experimental

4.1. General

All manipulations were carried out under exclusion of moisture in an inert nitrogen atmosphere and solvents were dried adequately and distilled prior to use. The NMR spectra were recorded on Bruker AVANCE 400 (^1H, ^{13}C 400 MHz) and DMX300 (^{29}Si 300 MHz) spectrometers. All chemical shifts are reported as δ values (ppm) relative to residual chloroform (δ_H 7.26), the central peak of $CDCl_3$ (δ_C 77.0) and tetramethylsilane (δ_{Si} 0.0). Elemental analyses were performed using a FLASH EA 1112 Microanalytical analyzer. Fourier transfer infrared spectra (FT-IR) were recorded with a Bruker TENSOR-27 IR spectrometer. GC-MS (EI) was measured by SHIMADZU (GC-MS-QP2010). Melting point was carried out in a WRS-1A digital melting point apparatus.

4.2. Synthesis of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane (*1*)

A mixture of 80.5 g $(Me_3Si)_2NH$, (0.5 mol) and 191.1 g (1.0 mol) $MePhSiCl_2$ was stirred at 120 °C under distillation of Me_3SiCl for over 12 h. After Me_3SiCl was totally distilled out, the mixture was cooled to room temperature. The crude product was distilled under vacuum (0.1 Torr) to give **1** (102.4 g 63%) as a colorless viscous liquid. Bp. 152 °C (0.1 Torr): ^1H NMR: δ 0.58, 0.65 [s, 6H, $Si(CH_3)$], 7.11–7.97 [m, 10H, $Si(C_6H_5)$], 1.95 [s, 1H, $HNSi_2$]. ^{13}C NMR: δ 3.13 [s,

2C, Si(CH_3)], 128.16–134.68 [m, 12C, Si(C_6H_5)]. ^{29}Si NMR: δ 2.66 [s, 2Si, ClSi(CH_3)(C_6H_5)].

4.3. Synthesis of 1,3-dichloro-1-methyl-1,3,3-triphenyldisilazane (**2**)

After a mixture of 50.6 g (0.2 mol) Ph_2SiCl_2 and 65.2 g (0.2 mol) **1** was maintained at a temperature of 160 °C for 8 h, an attempt to separate **2** was conducted. When the crude products were fractional distilled, **2** would disproportionate to give a series of fractions containing **1**, 1,3-dichlorotetraphenyldisilazane, chlorosilane and trimeric polysilazane. The distillates of **1**, **2** and chlorosilane were collected and after a second fractional distillation, 26.6 g (33%) of **2** was ultimately obtained with the purity of 88%, Bp. 186 °C (0.1 Torr): ^{1}H NMR: δ 0.62 [s, 3H, Si(CH_3)], 7.19–7.86 [m, 15H, Si(C_6H_5)], 2.26 [s, 1H, $HNSi_2$]. ^{13}C NMR: δ 3.52 [s, 1C, Si(CH_3)], 128.24–134.57 [m, 18C, Si(C_6H_5)]. ^{29}Si NMR: δ 3.20 [s, 1Si, ClSi(CH_3)(C_6H_5)], −7.93 [s, 1Si, ClSi(C_6H_5)$_2$].

4.4. Synthesis of 1,3-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (**3**) and 1,3-bis(chlorodiphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (**4**)

After 160 ml (0.4 mol) of 2.5 M *n*-Butyl lithium in hexane was added dropwise to a stirred solution of 130.4 g (0.4 mol) **1** in 600 ml toluene at 0 °C, the reaction mixture was allowed to rise steadily to refluxing temperature and stayed for 6 h. The precipitate of LiCl was filtered off quickly and the solvent was evaporated from the filtrate to give colorless crystal of **3** (85.5 g, 74%). Mp. 118.2–123.9 °C. ^{1}H NMR: δ 0.32, 0.34 and 0.36 [s, 6H, N_2Si(CH_3)], 0.52, 0.63, 0.75 [s, 6H, Si(CH_3)Cl], 7.23–7.89 [m, 20H, Si(C_6H_5)]. ^{29}Si NMR: δ −2.38 [s, 2Si, Si(CH_3)(C_6H_5)Cl], −2.98 and −3.59 [s, 2Si, N_2Si(CH_3)(C_6H_5)]. ^{13}C NMR: δ 0.76, 1.05 and 1.36 [s, 2C, N_2Si(CH_3)], 2.92 and 3.12 [s, 2C, Si(CH_3)Cl], 126.92–136.76 [m, 24C, Si(C_6H_5)]. IR (KBr): ν Si–Cl 503, 532 cm^{-1}; ν Si_4N_2 829, 1018, 1115 cm^{-1}. Anal. Calcd. for $C_{28}H_{32}Si_4N_2Cl_2$ (%): C, 58.00; H, 5.56; N, 4.83; Cl, 12.23. Found (%): C, 57.10; H, 5.61; N, 4.86; Cl, 12.45.

In the same manner described above, **4** was prepared from **2** (155.2 g, 0.4 mol) and 2.5 M *n*-Butyl lithium in hexane (160 ml, 0.4 mol) and isolated as a colorless crystal (91.2 g, 65%). Mp. 179.6–182.4 °C. ^{1}H NMR: δ 0.53 [s, 6H, N_2Si(CH_3)], 6.81–7.63 [m, 30H, Si(C_6H_5)]. ^{29}Si NMR: δ −14.80 [s, 2Si, Si(C_6H_5)$_2$Cl], −1.90 [s, N_2Si(CH_3)(C_6H_5)]. ^{13}C NMR: δ 1.40 [s, 2C, N_2Si(CH_3)], 127.62–137.34 [m, 36C, Si(C_6H_5)]. IR (KBr): ν Si–Cl 510, 541 cm^{-1}; ν Si_4N_2 828, 1016, 1116 cm^{-1}. Anal. Calcd. for $C_{38}H_{36}Si_4N_2Cl_2$ (%): C, 64.83; H, 5.25; N, 3.98; Cl, 10.07. Found (%): C, 64.54; H, 5.20; N, 4.05; Cl, 10.39.

4.5. Synthesis of 1,3-bis(hydroxymethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (**5**) and 1,3-bis(hydroxydiphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (**6**)

A solution of 124 g (0.15 mol) **3** in 200 ml diethyl ether was added to 120 ml of a mixture (H_2O: aqueous ammonia = 6:1 vol.%) in 200 ml diethyl ether at 0 °C. After vigorous stirring for 30 min, the mixture was shaken with water to remove the ammonia chloride and the solvent was distilled off under reduced pressure. The residue was recrystallized from the mixed solvent of diethyl ether and hexane to give **5** (38.21 g 47.0%) as white crystals. Mp. 106.3–108.2 °C. ^{1}H NMR: δ 1.72, [s, 2H, SiOH], 0.60 [s, 6H, N_2Si(CH_3)], 0.13 [s, 6H, Si(CH_3)OH], 7.09–7.58 [m, 20H, Si(C_6H_5)]. ^{29}Si NMR: δ −20.10 [s, 2Si, Si(CH_3)(C_6H_5)OH], −5.66 [s, 2Si, N_2Si(CH_3)(C_6H_5)]. ^{13}C NMR: δ 1.26 [s, 2C, N_2Si(CH_3)], 0.12 [s, 2C, Si(CH_3)OH], 127.32–138.84 [m, 24C, Si(C_6H_5)]. IR (KBr): ν Si–OH 3585 cm^{-1}; ν Si_4N_2 842, 1015, 1118 cm^{-1}. GC-MS m/z 542.96 (M^+, calcd for $C_{28}H_{34}Si_4N_2O_2$ 542.17). Anal. Calcd. for $C_{28}H_{34}Si_4N_2O_2$ (%): C, 61.94; H, 6.31; N, 5.16. Found (%): C, 61.99; H, 6.51; N, 4.94.

In the same manner described above, **6** was prepared from **4** (105.6 g, 0.15 mol) and isolated as a colorless crystal (87.9 g, 88%). Mp. 144.8–146.9 °C. ^{1}H NMR: δ 2.17, [s, 2H, SiOH], 0.64 [s, 6H, N_2Si(CH_3)], 7.2–7.8 [m, 30H, Si(C_6H_5)]. ^{29}Si NMR: δ −31.70 [s, 2Si, Si(C_6H_5)$_2$OH], −4.37 [s, 2Si, N_2Si(CH_3)(C_6H_5)]. ^{13}C NMR: δ 1.30 [s, 2C, N_2Si(CH_3)], 127.32–138.73 [m, 36C, Si(C_6H_5)]. IR (KBr): ν Si–OH 3584 cm^{-1}; ν Si_4N_2 843, 1014, 1118 cm^{-1}. GC-MS m/z 666.78 (M^+, calcd for $C_{38}H_{38}Si_4N_2O_2$ 666.20). Anal. Calcd. for $C_{38}H_{38}Si_4N_2O_2$ (%): C, 68.42; H, 5.74; N, 4.20. Found (%): C, 68.84; H, 5.89; N, 4.09.

4.6. Crystal structure determination of trans-**5** and trans-**6**

Single crystal of *trans*-**5** and *trans*-**6** suitable for X-ray crystallographic analyses were grown by slow evaporation of their respective solution in diethyl ether/*n*-hexane at room temperature. The diffraction experiments were carried out at 276 K on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using PROCESSAUTO program package, and absorption corrections were applied by the empirical method [33].

The structures were solved by direct method [34] using SIR92 and refined on F^2 (with all independent reflections) by the full-matrix least-squares technique using SHELXL97 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced at the positions calculated theoretically and treated with riding models. Details on crystal and intensity data collection are given in Table 1.

Table 1
X-ray diffraction data and structure refinement details for *trans*-**5** and *trans*-**6**.

Compound	*trans*-**5**	*trans*-**6**
Formula	$C_{28}H_{34}N_2O_2Si_4$	$C_{38}H_{38}N_2O_2Si_4$
fw (g mol^{-1})	542.93	667.06
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.512(3)	10.389(2)
b (Å)	9.789(3)	16.992(3)
c (Å)	16.040(5)	21.085(4)
α (°)	85.19(7)	70.27(3)
β (°)	83.57(7)	84.98(3)
γ (°)	87.68(6)	87.40(3)
V (Å^3)	1478.2(8)	3489.7(11)
Z	2	4
ρ (g cm^{-3})	1.220	1.270
Crystal size (mm)	0.31×0.26×0.20	0.32×0.28×0.05
Abs coeff (mm^{-1})	0.228	0.207
T (°C)	23	23
Radiation	Mo-Kα (λ= 0.71073 Å) graphite-monochromated	
2θ range(°)	1.28 ~ 25.34	1.03 ~ 25.38
Index ranges	$-11 \le h \le 11$ $-11 \le k \le 11$ $-19 \le l \le 19$	$-12 \le h \le 11$ $-19 \le k \le 20$ $-25 \le l \le 25$
No. of reflns collected	14,436	33,903
No. of indep. reflns.	5402 (R_{int} = 3.50%)	12758 (R_{int} = 8.43%)
Absorp. corr.	Numerical	Semi-empirical from equivalents
Transmission: t_{min}/t_{max}	0.9558/0.9326	1.0000/0.7623
Data/restraints/parameters	5402/0/329	12758/0/829
$R(F^2 > 2\sigma(F^2))$	0.0594	0.0807
$wR(F^2)$	0.1677	0.1846
Goodness-of-fit	1.222	1.081
Largest diff peak/hole (e Å^{-3})	0.506/−0.403	0.602/−0.447

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-804075 for *trans*-**6** and CCDC-804076 for *trans*-**5**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] W. Fink, J. Paint Technol. 42 (1970) 220–226.
[2] D.Y. Zhinkin, I.S. Shragin, V.M. Kopylov, et al., Vysokomol. Soed. Ser. A 22 (1980) 1541–1550.
[3] W. Fink, Angew. Chem. Int. Ed. 5 (1966) 760–776.
[4] D.Y. Zhinkin, I.S. Shragin, V.M. Kopylov, et al., Polym. Sci. U.S.S.R. 22 (1980) 1689–1699.
[5] W. Fink, Helv. Chim. Acta 51 (1968) 954–974.
[6] L.W. Breed, US 3702317 (1972).
[7] R.J. Perry, Organometallics 8 (1989) 906–910.
[8] Y.P. Zhu, L. Guo, Z.J. Zhang, et al., J. Appl. Polym. Sci. 103 (2007) 611–617.
[9] Z. Xie, Q. Li, J. Wang, Polym. Commun. 4 (1979) 215–223.
[10] Y.X. Xiao, D.Y. Son, Organometallics 23 (2004) 4438–4443.
[11] U. Wannagat, E. Bogusch, P. Geymayer, Mon. Chem. 102 (1971) 1825–1833.
[12] L.W. Breed, W.L. Budde, R.L. Elliott, J. Organomet. Chem. 6 (1966) 676–679.
[13] L.W. Breed, R.L. Elliott, J.C. Wiley, J. Organomet. Chem. 24 (1970) 315–325.
[14] G.H. Wiseman, D.R. Wheeler, D. Seyferth, Organometallics 5 (1986) 146–152.
[15] U. Wannagat, S. Klemke, Mon. Chem. 110 (1979) 1089–1097.
[16] E. Duguet, M. Schappacher, A. Soum, J. Organomet. Chem. 458 (1993) 9–12.
[17] L.W. Breed, R.L. Elliott, J.C. Wiley, J. Organomet. Chem. 31 (1971) 179–185.
[18] W. Fink, Helv. Chim. Acta 51 (1968) 1743–1750.
[19] L.W. Breed, J.C. Wiley, Inorg. Chem. 11 (1972) 1634–1638.
[20] X.J. Bao, M.J. Edirisinghe, J. Mater. Chem. 10 (2000) 395–401.
[21] E. Bacqué, J.-P. Pillot, M. Birot, et al., J. Organomet. Chem. 481 (1994) 167–172.
[22] J. Silbiger, J. Fuchs, Inorg. Chem. 4 (1965) 1371–1372.
[23] W. Fink, Helv. Chim. Acta 52 (1969) 1833–1841.
[24] U. Wannagat, Mon. Chem. 102 (1971) 1806–1816.
[25] W. Fink, Helv. Chim. Acta 51 (1968) 1011–1028.
[26] S. Bartholmei, U. Klingebiel, G.M. Sheldrick, et al., Z. Anorg. Allg. Chem. 556 (1988) 129–140.
[27] L.W. Breed, R.L. Elliott, Inorg. Chem. 3 (1964) 1622–1627.
[28] S.N. Gurkova, A.I. Gusev, N.V. Alekseev, et al., J. Struct. Chem. 22 (1981) 142–145.
[29] S.N. Gurkova, A.I. Gusev, N.V. Alekseev, et al., J. Struct. Chem. 19 (1978) 164–166.
[30] B. Jaschke, R. Herbst-Irmer, U. Klingebiel, et al., J. Chem. Soc. Dalton Trans. 18 (1998) 2953–2954.
[31] B. Jaschke, R. Herbst-Irmer, U. Klingebiel, et al., J. Chem. Soc. Dalton Trans. 12 (2000) 1827–1828.
[32] L. Parkanyi, G. Argay, P. Hencsei, et al., J. Organomet. Chem. 116 (1976) 299–305.
[33] T. Higashi, ABSCOR-Empirical Absorption Correction Based on Fourier Series Approximation. Rigaku Corporation, Tokyo, 1995.
[34] A. Altomare, G. Cascarano, C. Giacovazzo, et al., J. Appl. Crystallogr. 27 (1994) 435.